



The influence of the preparation procedure on the storage and regeneration behavior of Pt and Ba based NO_x storage and reduction catalysts

Anna Lindholm^{a,b}, Neal W. Currier^c, Jazaer Dawody^a, Arif Hidayat^{a,b}, Junhui Li^c, Aleksey Yezerets^c, Louise Olsson^{a,b,*}

^a Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^b Chemical Reaction Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^c Cummins Inc., 1900 McKinley Ave, MC 50183, Columbus, IN 47201, USA

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ABSTRACT

The influence of the preparation procedure on the performance of NO_x storage and reduction catalysts was investigated by means of flow reactor experiments. Three catalysts were examined; one Pt/Al and two Pt/Ba/Al samples. One of the Pt/Ba/Al samples was prepared with Pt impregnated on Al/Ba and one with Ba impregnated on Al/Pt. The results clearly show that the preparation procedure influences the behavior of NO_x storage and reduction catalysts both during lean and rich conditions. The order of the impregnation steps is crucial especially at higher temperatures; a higher storage capacity is obtained when impregnating Al/Pt with Ba than when impregnating Al/Ba with Pt. The storage increased with as much as 54% when adding Ba in the last step. The N₂O and NH₃ formation is also affected by the preparation procedure; there is a clear dependency on the order of impregnation steps. Moreover, N₂O is not only formed during rich conditions but also in the beginning of the lean period over the Pt/Al and Al/Pt/Ba samples.

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1. Introduction

NO_x storage and reduction (NSR) catalysts can reduce NO_x emitted from lean burn engines, such as the diesel engine and lean burn gasoline engines. This technique was proposed by Toyota in the 1990s [1]. The nitrogen oxides are stored in the catalyst during lean operation. In order to retain the storage capacity of the catalyst it has to be regenerated periodically from the NO_x stored and this is done during short rich periods, where the exhausts are oxygen deficient. During the rich conditions the NO_x adsorbed is released and reduced into N₂ and possibly undesired byproducts. The NSR catalyst contains a high surface area support, typically γ -alumina, on which storage components and precious metals are deposited. The storage components are usually an alkali or alkali-earth metal compound such as barium and the precious metals are

commonly Pt, Pd or Rh. The NSR catalyst that has gained the most attention in the literature is the Pt/Ba/Al catalyst.

Several publications have investigated the storage of NO_x [2–13] and lately the interest in the regeneration of the NSR catalysts has increased. Hence, more effort has been put in the research of the regeneration period [14–22]. It is notable that the catalysts studied are prepared in different ways. This probably affects the behavior of the catalysts and may influence the conclusions about the performance of the NSR catalysts. In the investigations various Pt precursor such as Pt(NH₃)₄(OH)₂ [12,13,23], Pt(NH₃)₂(NO₂)₂ [4–6,11,16,23–26], H₂Pt(Cl)₆ [7,21,23], and Pt(NO₃)₂ [22,23,27–29] have been used for the Pt impregnation and the precursors for barium impregnation was either Ba(Ac)₂ [4–6,11,16,24–26,30] or Ba(NO₃)₂ [7,12,13,21–23,27–29,31]. Dawody et al. [23] studied the effect of the type of Pt precursor on the NO_x storage and reduction activity and showed that the sample prepared using platinum nitrate was the most active catalyst. In addition, the effect of Ba-loading has been the focus of several publications [3–8] and the general conclusion is that the higher the Ba loading the higher the storage capacity. Recently, Piacentini et al. [26] investigated the effect of the preparation method on the behavior

* Corresponding author at: Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. Fax: +46 31 772 4390.

E-mail address: louise.olsson@chalmers.se (L. Olsson).

of NSR catalysts by comparing Pt/Ba/Al catalyst prepared by the wet impregnation method with catalysts prepared by a flame spray pyrolysis method. However, the most common method to deposit the active materials is by wet impregnation. The catalyst components are usually impregnated by either adding Ba to a Pt/Al sample [4–6,11,16,21,25,26,28,29] or by adding Pt to a Ba/Al sample [7,12,13,22,23,27,30]. However, to our knowledge no studies concerning the order of the impregnation steps in conventional wet impregnation methods have been published. In this study we have examined the effect of the preparation procedure on the behavior of Pt and Ba based NSR catalysts by using the conventional wet impregnation method. More specifically we have varied the order of the impregnation steps in the preparation procedure, either by adding Pt to the catalyst before impregnating it with Ba or by adding Ba before adding Pt to the sample. The objective with this study was to gain a better understanding of the storage of NO_x and the regeneration, including the production of by products such as N₂O and NH₃. By studying different catalysts the individual effects of the different components in NSR catalysts on both the storage and regeneration process can be clarified.

2. Experimental

2.1. Catalyst preparation

Three model catalysts are examined in this study; two catalysts with platinum, barium and alumina and one catalyst with platinum and alumina. The catalysts are monolith samples with a cell density of 400 cpsi. All samples have the same dimensions; the length is 30 mm and the diameter is 21 mm. Table 1 presents the catalysts and their washcoat compositions. All catalysts were prepared by first impregnating cordierite (2MgO·2Al₂O₃·5SiO₂) monoliths with γ-Al₂O₃. The monoliths were immersed in either of the slurries and the excess liquid was removed by carefully blowing air through the monoliths. Thereafter the monoliths were dried in air at 95 °C which was followed by calcination in air at 500 °C for 2 min. This procedure was repeated until the intended amount of alumina was applied to the samples. As a last step the samples were calcined in air at 600 °C for 2 h.

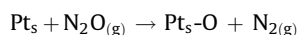
Platinum was added after the alumina impregnation to samples 1 and 2. Incipient wetness impregnation was used to apply platinum to the catalysts, which here implies filling the monolith channels with an aqueous solution of Pt(NO₃)₂ and letting the samples dry in air at 80 °C for 12 h. The samples were then calcined in air at 550 °C for 2 h. Sample 1 was then applied with barium and the same procedure as for the alumina impregnation was used. The precursor for barium was a Ba(NO₃)₂ solution.

A different order of applying the catalyst components was used for sample 3, although the procedure of the individual impregnation steps was kept the same. Barium was added after the alumina and platinum was then added as a last step to these samples. The catalysts are denoted as in the order of the impregnation steps (see Table 1), i.e. the sample denoted Al/Pt/Ba is prepared by first impregnating the monolith with alumina, which is followed by Pt impregnation and finally by adding barium to the catalyst.

2.2. Catalyst characterization

The specific surface area of the samples was determined by nitrogen adsorption at 77 K according to the BET method. A Micromeritics ASAP 2010 instrument was used to measure the surface areas which are presented in Table 1.

The Pt dispersion of the catalysts was estimated by performing N₂O dissociation over the samples. Nitrous oxide dissociates over Pt, and oxygen occupies each Pt site according to the following reaction:



where Pt_s denotes a surface Pt atom [32]. The stoichiometry for Pt_s to N₂ is 1:1, hence the Pt dispersion can be calculated by integrating the N₂ signal during the N₂O exposure step [27]. The flow reactor used to estimate the Pt dispersion of the catalysts was equipped with a Balzer QME 125 mass spectrometer. Prior to each experiment, the catalyst was pretreated at 500 °C for 10 min with 1% O₂ in Ar, followed by 5 min of 100% Ar and thereafter 10 min of 2% H₂ in Ar. After the pretreatment the catalyst was cooled to 90 °C and exposed to 500 ppm N₂O. The Pt dispersions of the samples are presented in Table 1.

2.3. Activity measurements

The experiments conducted in this study were performed in a flow reactor consisting of a horizontal quartz tube with an insulated heating wire. The total flow rate used in all measurements were 3500 ml/min (SV = 20,200 h⁻¹). Argon was used as the carrier gas in the experiments. Two thermocouples were used to measure and control the temperature; one thermocouple was placed about 10 mm in front of the catalyst and the other was placed inside the catalyst, 10 mm from the rear end. The outlet NO concentrations were analyzed by a chemiluminescence NO_x detector (CLD 700), the outlet N₂O signal by a non-dispersive IR Mairhak UNOR 610 N₂O analyzer, and the outlet NO₂ and NH₃ concentration by a gas FTIR (Bio-Rad FTS 3000 Excalibur Spectrometer with a Specac Sirocco series heatable gas cell, P/N 24102, with a 2 m path length and a volume of 0.19 l). Before every experiment the samples were pretreated at 500 °C with 10 min of 8% O₂ in Ar followed by 5 min of 100% Ar and finally the samples were reduced in 1.8% H₂ for 10 min.

Transient NO_x storage and reduction cycles were conducted at 200 °C, 300 °C and 400 °C over the three catalysts. The composition of the lean gas mixture in the NO_x storage and reduction cycles was 300 ppm NO and 8% O₂ and the feed contained 300 ppm NO and 8000 ppm H₂ during rich conditions. Three lean/rich (4 min/1 min) cycles were performed in each experiment. We have chosen to show results from the third cycles throughout this paper, since the first cycles for can store more NO_x due to the high temperature pretreatment before the first cycle.

Temperature programmed desorption (TPD) experiments were conducted on the Al/Pt and Al/Pt/Ba samples. The samples were exposed to 300 ppm NO₂ at 200 °C, 300 °C or 400 °C for 60 min, followed by flushing the samples with Ar only for 15 min. After that was a temperature ramp conducted with a speed of 10 °C/min to about 520 °C.

Table 1
Sample washcoat compositions, BET surface area and platinum dispersion.

Sample nr.	Sample	Washcoat (mg)	wt% Pt	wt% Ba	BET (m ² /g _{washcoat})	Pt dispersion (%)
1	Al/Pt/Ba	1040	2.9	20.8	97	18
2	Al/Pt	1080	2.9	–	160	20
3	Al/Ba/Pt	993	3.2	20.7	137	25

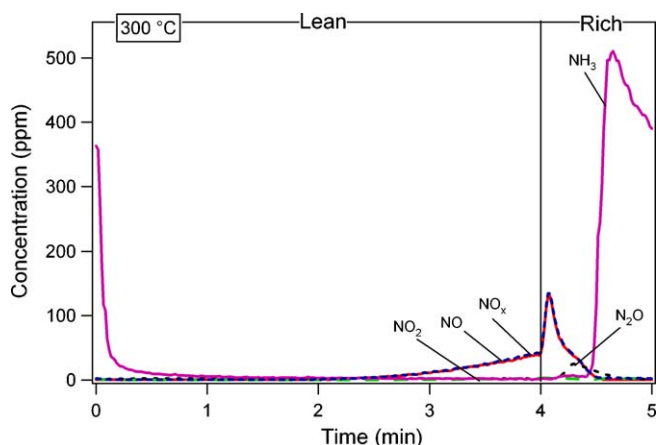


Fig. 1. Outlet NO, NO₂, NO_x, N₂O and NH₃ concentrations from one lean/rich cycle conducted over catalyst 1 (Al/Pt/Ba) at 300 °C. The gas composition during lean was 300 ppm NO and 8% O₂ and the composition during rich was 300 ppm NO and 8000 ppm H₂.

3. Results

Fig. 1 shows a characteristic NO_x storage and reduction cycle for the catalysts examined. In this figure the outlet NO, NO₂, NO_x, N₂O, and NH₃ concentrations from one lean/rich cycle conducted at 300 °C over the Al/Pt/Ba catalyst is presented. The gas composition contained 300 ppm NO and 8% O₂ during lean conditions and 300 ppm NO and 8000 ppm H₂ during rich conditions. The catalyst possesses a high storage capacity with a complete uptake of NO_x for approximately 2.5 min. After 4 min of lean conditions the gas mixture is switched into rich conditions which results in a release of NO from the catalyst. As can be seen in the figure N₂O and NH₃ are formed during the rich period. Nitrogen oxides are first reduced into N₂O and then into NH₃. The maximum N₂O concentration is 40 ppm for this catalyst at this temperature. The NH₃ signal is observed 30 s after the switch from lean and it rises above of the inlet NO_x concentration. The NH₃ concentration then falls off and at the end of the rich period all incoming NO_x is converted into NH₃. There is also likely a N₂ production in the rich period, but N₂ was not measured in this work. This is further discussed in Section 4.

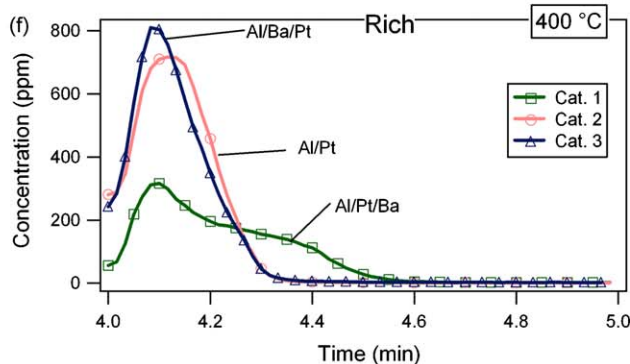
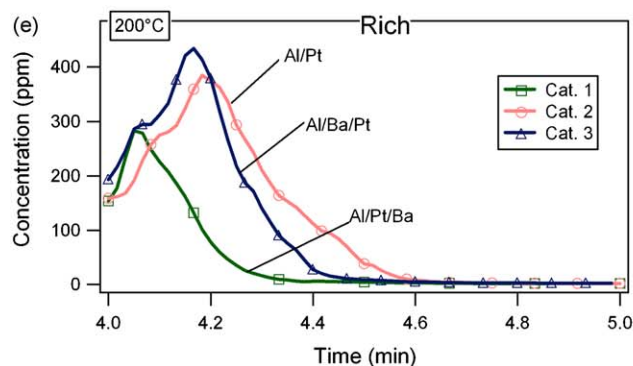
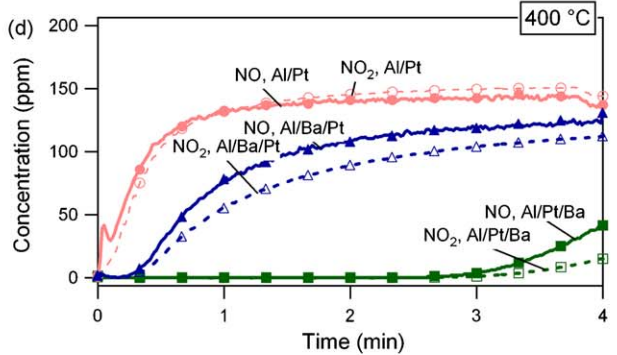
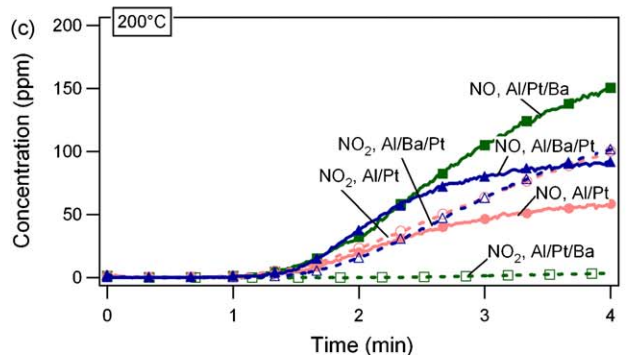
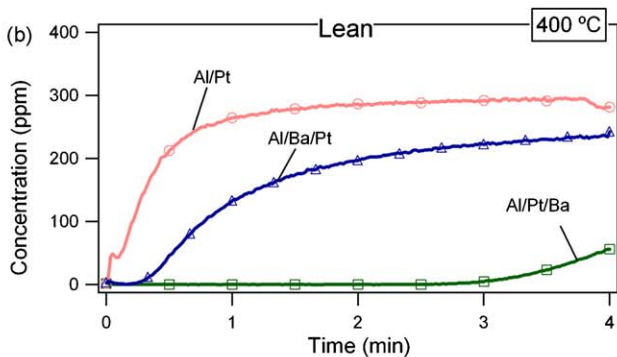
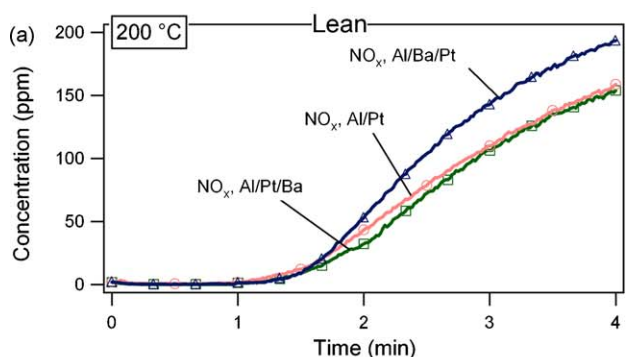


Fig. 2. (a and b) Measured NO_x concentrations at 200 °C and 400 °C from all catalysts examined during lean conditions (300 ppm NO and 8% O₂), (c and d) the NO and NO₂ concentration, and (e and f) the NO_x concentrations during rich conditions (300 ppm NO and 8000 ppm H₂).

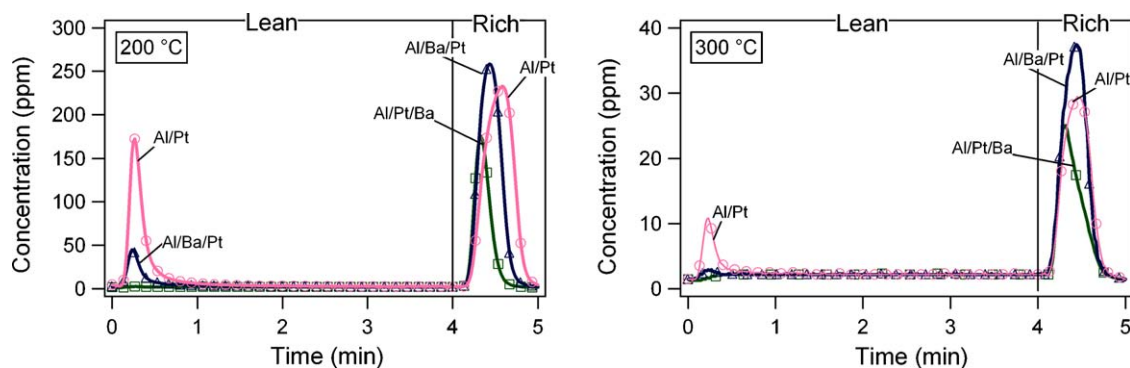


Fig. 3. Measured N_2O concentrations at 200 °C and 300 °C from all catalysts examined. The gas mixture contained 300 ppm NO and 8% O_2 during lean conditions and 300 ppm NO and 8000 ppm H_2 during rich conditions.

3.1. NO_x storage and release

A comparison of the NO_x curves at 200 °C and 400 °C from all catalysts examined is shown in Fig. 2. The upper panels (a) and (b) show the NO_x concentrations obtained from the lean period, in the middle panels are the NO and NO_2 levels shown and the lower panels show the NO_x release curves from the rich period. It can be seen that all catalysts have a high storage capacity at 200 °C. The complete uptake of NO_x occurs for at least 40 s for the catalysts. The Al/Pt samples show a high storage capacity at 200 °C. However, the NO_x concentrations obtained at 400 °C from Al/Pt catalysts show that there is no total uptake during lean conditions; instead the concentration rises immediately when the lean period begins. At 200 °C the best storage capacity is achieved by the Al/Pt/Ba sample. However, the storage is quite similar for all samples at this temperature. The NO_x breakthrough for these catalysts occurs after about 1–1.5 min of complete uptake. At 400 °C, on the other hand, the order of the preparation steps is more important. The catalysts with barium added as a last step in the preparation procedure have a much higher storage capacity than when barium is added before platinum. The total uptake of NO_x for the Al/Pt/Ba catalysts occurs for at least 2 min more than for the Al/Ba/Pt samples. The Al/Pt/Ba catalyst has a total uptake of 3 min. A similar storage behavior is observed at 300 °C (not shown here). Moreover, the lower panels in Fig. 2 show the NO_x release for the three catalysts. It is clear that the amount of released NO_x is lower for the Al/Pt/Ba samples compared to the other samples, even though this samples adsorb the most NO_x .

3.2. N_2O formation

The outlet N_2O concentrations from the three catalysts examined are shown in Fig. 3 for 200 °C and 300 °C. Nitrous oxide is formed to a larger extent at 200 °C than at 300 °C. The highest

N_2O concentration observed is 272 ppm at 200 °C and 38 ppm at 300 °C and occur for the Al/Ba/Pt sample. A very low amount of N_2O is formed at 400 °C (not shown here). Only the Al/Pt/Ba sample forms a significant amount of N_2O at 400 °C; the N_2O concentration detected over this sample is about 20–30 ppm. The N_2O concentration detected from all other samples is within the same range as the experimental error.

It can be seen that the preparation procedure affects the performance of the N_2O formation of the barium containing samples. The catalyst with Ba added before Pt gives the highest amount of N_2O . The results from the measurement conducted over the Al/Pt samples reveal that N_2O is not only formed during rich conditions over these catalysts but also in the beginning of lean period. The amount of N_2O formed during lean conditions is lower than the amount produced under rich conditions. This is also seen for the Al/Ba/Pt sample, but not for the Al/Pt/Ba. In addition, the shape of the curves is similar for both samples during the lean and the rich period.

3.3. NH_3 formation

Fig. 4 presents the measured NH_3 concentrations observed during the rich periods at 200 °C, 300 °C and 400 °C over the three catalysts examined. The amount of formed NH_3 is the largest at 200 °C for all samples studied. In most measurements the NH_3 concentration overshoots the inlet NO_x concentration and this occurs to the largest extent at 200 °C, where the maximum NH_3 concentration reaches above 1400 ppm. Further, it can be seen that the ammonia signal is not detected immediately when switching to rich conditions. A delay of at least 0.2 min is observed for all samples.

Also for the NH_3 formation of the barium containing samples there is a dependency on the order of impregnation in the preparation procedure. At 400 °C the NH_3 from the Al/Ba/Pt sample

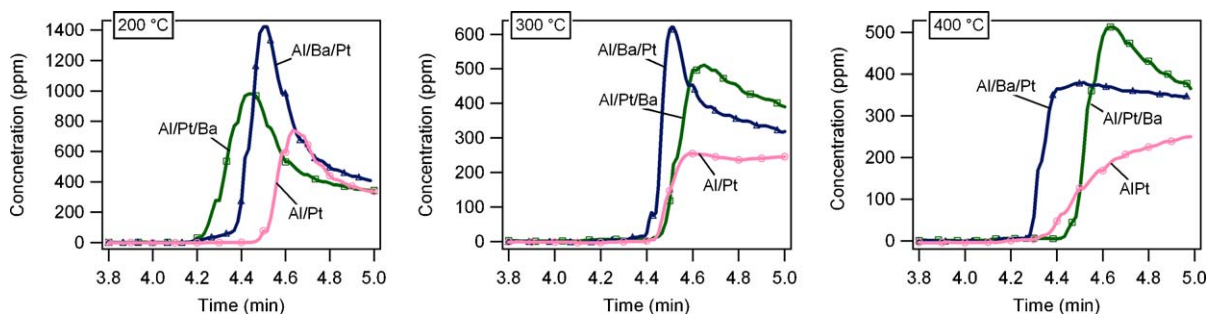


Fig. 4. Measured NH_3 concentrations at 200 °C, 300 °C and 400 °C from all catalysts examined. The gas mixture contained 300 ppm NO and 8% O_2 during lean conditions and 300 ppm NO and 8000 ppm H_2 during rich conditions.

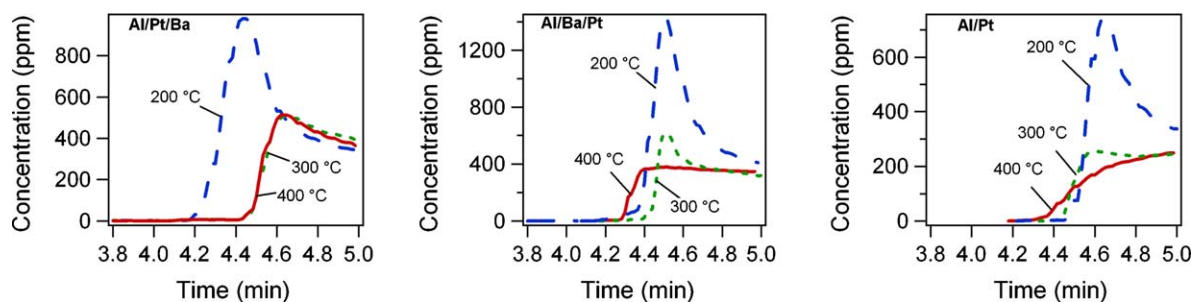


Fig. 5. Temperature dependency of NH_3 formation for all catalysts examined. The gas mixture contained 300 ppm NO and 8% O_2 during lean conditions and 300 ppm NO and 8000 ppm H_2 during rich conditions.

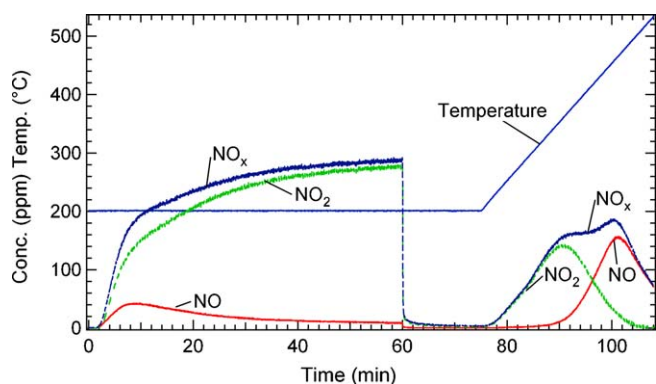


Fig. 6. TPD experiment on the Al/Pt/Ba catalyst. The sample was exposed to 300 ppm NO_2 at 200 °C for 60 min, which was followed by a period with Ar only and increasing the temperature to about 520 °C, with a speed of 10 °C/min.

breaks through around 0.3 min after the switch to rich conditions, which is 0.2 min before the breakthrough of NH_3 from the Al/Pt/Ba sample. In addition, the former sample does not exhibit the typical overshoot curve that both the latter sample shows. The features of the NH_3 curves from the Al/Pt/Ba and Al/Ba/Pt samples are the same also at the lower temperatures. However, the timing of the ammonia evolution differs.

The temperature dependency of the ammonia formation was investigated by plotting the NH_3 signals from the temperatures studied in one graph for each catalyst. The results are presented in Fig. 5. From the figure it is clear that the order of the impregnation steps influences the time of the NH_3 evolution. Ammonia is detected earliest at 200 °C when barium is added after the Pt impregnation. At this temperature there is a delay of only 0.2 min for the ammonia signal. The delay is larger for the ammonia signals from the measurements conducted at 300 °C and 400 °C, which are

observed at approximately the same time for both samples. In contrast to these results, the observations from the Al/Ba/Pt samples reveal that the shortest delay of the ammonia signal is detected at 400 °C and the longest at 300 °C. The results from the Al/Pt samples show that the delay is around 0.4 min for all temperatures examined.

3.4. TPD experiments

In order to investigate the stability of the formed nitrates temperature programmed desorption experiments were conducted over the Al/Pt/Ba and Al/Pt samples at 200, 300 and 400 °C. The samples were exposed to 300 ppm NO_2 for 60 min, then the catalyst was flushed with Ar only and this was followed by a temperature ramp to about 520 °C. In Fig. 6 are the results from the NO_2 TPD at 200 °C over the Al/Pt/Ba showed. Initially, we observe a total uptake of NO_x for about 2 min, which is similar to the cycling experiments shown in Fig. 2. This is followed by a breakthrough of NO_2 and a simultaneous production of NO . When increasing the temperature while exposing the catalyst to Ar there is a release of NO_x . Two peaks are visible, with their maximum at 360 °C and 440 °C, respectively. Initially the NO_x desorption peak consist mainly of NO_2 , but at higher temperatures mainly NO .

In Fig. 7 is a comparison of the released NO_x during the temperature ramps for Al/Pt/Ba and Al/Pt. The TPD conducted at 200 °C is shown in Fig. 7a and shows that the stability of the NO_x on Al/Pt is much less than for the Al/Pt/Ba. Further only one desorption peak is observed for the Al/Pt sample (290 °C), but two are visible for the Al/Pt/Ba sample (360 °C and 440 °C). In Fig. 7b, are the results from the TPD at 400 °C displayed, which show that there is still a large storage on the Al/Pt/Ba, with a maximum peak of 130 ppm. However, the storage on the Al/Pt is very small at this temperature, with a maximum peak of about 15 ppm.

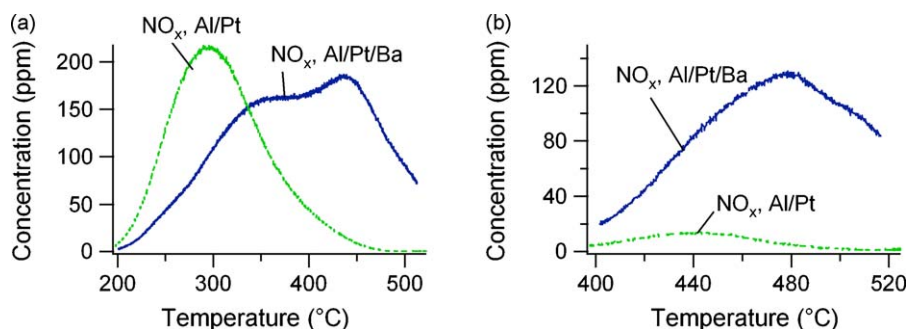


Fig. 7. TPD experiment on Al/Pt/Ba and Al/Pt at (a) 200 °C and (b) 400 °C. The samples were exposed to 300 ppm NO_2 for 60 min, which was followed by a period with Ar only and increasing the temperature to about 520 °C, with a speed of 10 °C/min.

4. Discussion

4.1. NO_x storage

This study clearly shows that the preparation procedure influences the behavior of NO_x storage and reduction catalysts both during lean and rich conditions. A very interesting feature observed here is that the storage capacity of the barium containing samples is significantly affected by the order of the impregnation steps in the preparation. The storage capacity at 300 °C and 400 °C is much higher when barium is added after the platinum impregnation compared to when adding barium before adding platinum to the catalysts (Fig. 2). At 400 °C the storage increases with as much as 54%.

Both the barium and alumina can store large amounts of NO_x [29,33], which we also observe in this study. The NO₂ TPD experiments conducted on Al/Pt/Ba and Al/Pt shows that the stability of the NO_x is much lower on the Al/Pt compared to on Al/Pt/Ba (Fig. 7). This is consistent with the amount of NO_x stored during the lean cycle, which is shown in Fig. 8. The Al/Pt sample has an optimum storage temperature at 200 °C and only stores minor amounts at 400 °C, while the Al/Pt/Ba has a maximum storage at 300–400 °C. This is consistent with the literature, where it is reported that barium containing catalysts have an optimum temperature for NO_x storage of about 350–400 °C [3,34,35]. The NO₂ TPD experiments conducted at 400 °C (Fig. 7b), also show that the Al/Pt catalyst stores very little at this high temperature, with a maximum of NO_x of only 15 ppm. However, the Al/Pt/Ba has a maximum NO_x peak of 150 ppm.

Another difference between the Al/Pt and Al/Pt/Ba sample is that in the 200 °C TPD experiments (Fig. 7a) the Al/Pt only gives one desorption peak, but the Al/Pt/Ba have two. In the literature several authors state that there are multiple storage sites available in Pt and Ba containing catalysts [3,10,21,30,36,37]. Also in our detailed kinetic model we found it necessary to include two different NO_x storage sites [38] in order to explain the experimental features, where one site contained NO_x species with low temperature stability and one for high temperature stable species. One possible explanation for the multiple storage site in the Al/Pt/Ba is storage on both barium and alumina sites, where the NO_x on the alumina sites have a lower stability. According to Fanson et al. [7] about 8–10 wt% BaO forms a monolayer of barium on the alumina. However, a recent study by Yi et al. [39] showed that the coverage of one monolayer of barium was significantly underestimated by Fanson et al. [7]. According to Yi et al. [39] 8 wt% BaO only gives 0.26 ML and 20 wt% about 0.75 ML. Thus, in our catalysts with

20 wt% there are significant amounts of alumina sites still available. In addition, it is likely that some barium particles are present [36], which would even further increase the available alumina surface. Further, Dawody et al. [23] observed with FTIR that barium do not cover all the alumina sites. This is in line with in-situ FTIR results from Westerberg and Fridell [37] who assign some of the peaks to be nitrates on alumina in close contact with the barium. In our previous study [29], we also propose that that alumina contributes to the overall storage capacity of Al/Pt/Ba catalysts based on flow reactor experiments. It is also possible that there is a difference in stability of surface nitrates and bulk nitrates, as proposed by Szanyi et al. [36] and we suggest that the reason for the multiple storage sites is a combination of surface and bulk species on the barium and also storage on the alumina. Thus, the low temperature stable NO_x species comes both from storage on surface barium sites as well as alumina.

In an earlier publication [29] we investigated the influence of water and CO₂ on the NO_x storage and reduction on the Al/Pt/Ba catalyst and also on a Pt/Al₂O₃ sample, similar to the one used in this study. We observed that there was only a small decrease in NO_x storage when adding CO₂ to the gas mixture for the Pt/Al₂O₃ catalyst. However, a significant decrease was observed when adding H₂O to the feed gas for the Pt/Al₂O₃, which also Toops et al. [40] observed. The result when having a combination of H₂O + CO₂ was similar to the case for H₂O and this was observed for all temperatures investigated (100 °C, 200 °C, 300 °C and 400 °C). Thus, the NO_x storage on alumina is mostly affected by H₂O, due to the formation of hydroxyl groups [40]. However, it should be pointed out that there is still a significant storage available on alumina also with water present. The storage decreased 48% at 100 °C, 18% at 200 °C, 46% at 300 °C and 64% at 400 °C when adding water to the feed compared to dry conditions [29]. For the Al/Pt/Ba sample at 400 °C we only observe a small effect of water (reduction by 6%), but the storage is significantly decreased when using CO₂ (with 33%). We suggest that the reason is the formation of barium carbonates that decreases the NO_x storage when CO₂ is present [10,30]. The effect of water on the NO_x storage increases when decreasing the temperature and the reduction of NO_x storage is 9% at 300 °C and 22% at 200 °C. The opposite trend is observed for CO₂, i.e. the influence of CO₂ is decreased when decreasing the temperature (a reduction by 12% at 300 °C). Thus, for the Al/Pt/Ba catalyst the storage is mostly influenced by CO₂ at high temperature and by H₂O at low temperature. These results imply that at low temperature the storage of NO_x occurs not only on the barium but also on the alumina and at high temperatures the storage occurs mainly on barium sites [29].

The dispersion of the platinum in Al/Ba/Pt and Al/Pt/Ba are both close to 20%. However, the storage of the two samples differs significantly. The Al/Ba/Pt catalyst had its maximum storage at 200–300 °C, compared to 300–400 °C for the Al/Pt/Ba (Fig. 8) and it also stores significantly less. At 400 °C the storage was decreased with as much as 55% for the case when barium was added before Pt. The maximum storage at a low temperature is more similar to the Al/Pt catalyst (maximum storage at 200 °C). In respect to the amount of NO_x stored the Al/Ba/Pt is between the Al/Pt and the Al/Pt/Ba/sample (Fig. 8). We therefore suggest that the barium is not well utilized when impregnating Al/Ba with Pt compared to when impregnating Al/Pt with Ba, resulting in more storage on the alumina for the Al/Ba/Pt catalyst and less storage on the barium. This explains the low storage at 400 °C, where the storage on the barium is important and the relative large storage at low temperature where storage on alumina likely is important. It is known that barium can dissolve in aqueous solutions [23] and it is possible that the barium added before the Pt impregnation could dissolve when the catalysts were soaked in the acidic Pt(NO₃)₂

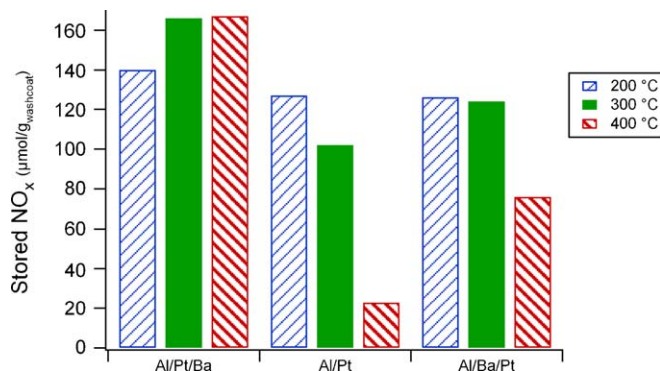


Fig. 8. The amount of stored NO_x [μmol/g_{washcoat}] calculated for each catalyst at all temperatures examined. The gas composition of the 4 min long lean period was 300 ppm NO and 8% O₂.

solution. However, when preparing the Al/Ba/Pt catalysts examined here the catalysts did not lose any weight after the Pt impregnation. Nevertheless, it is likely that the acidic $\text{Pt}(\text{NO}_3)_2$ solution affects the barium deposited on the alumina support and makes the barium less available for NO_x storage. It is possible that the barium particles reconstruct and forms larger aggregates, and less sites will be available for storage. The BET surface area for the three samples, see Table 1, show that the Al/Pt sample has the highest area ($160 \text{ m}^2/\text{g}$) and that it is decreased for the Al/Pt/Ba to $97 \text{ m}^2/\text{g}$. In several earlier studies it has been shown that the surface area is significantly lower for Pt/Ba/Al compared to Pt/Al [27,41]. Szailer et al. [41] observed that the BET surface area decreased when the barium loading increased and suggested that barium fills some pores of the alumina causing the decrease in surface area. Interestingly, the Al/Ba/Pt shows a higher surface area ($137 \text{ m}^2/\text{g}$) than the Al/Pt/Ba ($97 \text{ m}^2/\text{g}$). Dawody et al. [27] obtained surface areas between $130 \text{ m}^2/\text{g}$ and $140 \text{ m}^2/\text{g}$, for catalysts prepared with a similar method as the Al/Ba/Pt. As discussed above, based on the storage behavior for the Al/Ba/Pt, we propose that the barium is better dispersed for the Al/Pt/Ba catalyst. We suggest that the lower surface area of Al/Pt/Ba is due to a higher proportion of alumina covered by the barium and at the same times blocks more pores, resulting in a further decrease in the BET surface area in the same way as Szailer et al. [41] observed when increasing the barium loading.

When examining all lean rich cycles we observe that the cycles are quite similar at 300°C and 400°C and that is also the case for Al/Pt at 200°C . For Al/Ba/Pt at 200°C the total uptake in the first cycle is about 100 s and in the third cycle 90 s and the NO_x concentration in the end of the lean period is 140 ppm and 190 ppm, respectively. However, for the Al/Pt/Ba at 200°C there is a significant difference, the first cycle has a total uptake of 170 s, which decreases to 90 s in the third cycle and the NO_x concentration in the end of the lean period increases from 45 ppm to 155 ppm. After the third cycle the results are similar for all catalysts. We propose that the reason is differences in nitrate stability of the catalysts. The nitrates are less stable on alumina, which results in that the nitrates are easily reduced at this low temperature, resulting in similar lean cycles. For the Al/Pt/Ba there is also a formation of barium nitrates, which are more stable as shown in the NO_2 TPD experiments (Fig. 7). Since the nitrates are more stable they are more difficult to reduce at this low temperature, which causes the storage to decrease significantly between the first and third cycle. The Al/Ba/Pt only has a small decrease in storage capacity between the first and third cycle and thus behaves similar to the Al/Pt catalyst. As stated above we propose that the reason is that the barium is poorly dispersed on this catalyst and a large part of the storage at 200°C occurs on alumina for this catalyst.

4.2. NO_x release and reduction

The results from the NO_x release curves (Fig. 2) showed that the amount of NO_x released was the lowest for the Al/Pt/Ba sample, even at 400°C where this sample stores significantly more than the others. The selectivities for N_2 and NH_3 production are shown in

Table 3

NH_3 selectivity at 200°C , 300°C , and 400°C .

Sample	200°C (%)	300°C (%)	400°C (%)
Al/Pt/Ba	30	17	16
Al/Pt	18	10	8
Al/Ba/Pt	32	17	18

Tables 2 and 3 and is calculated according to

$$S_{\text{N}_2} = \frac{\text{NO}_{x,\text{feed}} - (\text{NO}_x + \text{NH}_3 + 2\text{N}_2\text{O})}{\text{NO}_{x,\text{feed}}} \quad (1)$$

$$S_{\text{NH}_3} = \frac{\text{NH}_3}{\text{NO}_{x,\text{feed}}} \quad (2)$$

The selectivity to NH_3 (Table 3) is between 10% and 30% and the reason for these high values is the long rich period. The objective with using such a long rich period was to remove as much NO_x as possible. In a practical application the rich period would of course be shorter, resulting in a decreased selectivity to NH_3 and an increased for N_2 . The selectivity to form N_2 is the highest for the Al/Pt/Ba for all temperatures investigated and at 400°C it is 74%, which should be compared with 12% and 27% for Al/Pt and Al/Ba/Pt. One reason for the low N_2 selectivity for the two latter is due to the low NO_x storage at 400°C . At 200°C the three catalysts stores similar amounts of NO_x (Fig. 2), but the N_2 selectivity is still much higher on Al/Pt/Ba than on Al/Ba/Pt. We propose that the reason for the lower NO_x peak in the initial part of the rich period and the high N_2 selectivity for the Al/Pt/Ba sample is due to a higher reduction efficiency of the platinum in Al/Pt/Ba. The reason can be a higher activity of platinum, proximity between platinum and barium or a combination between the two.

We have previously observed that the activity of Pt supported on alumina is much higher than for Pt supported on Ba/Al [42]. This is in line with the study by Takahashi et al. [43], who observed that the HC oxidation on the noble metals decreases when the alkalinity of the support increases. In Al/Pt/Ba the Pt is supported on alumina and not on Ba/Al which may explain a higher reduction capacity. Further, several publications have stressed that the proximity between the noble metal and the storage components is very important for NO_x storage [1,3,4,24,25,30]. As discussed above, the barium might be better dispersed on the Al/Pt/Ba catalyst, which caused the lowering of the BET surface. If it is more dispersed the contact between the barium and Pt is probably better, which would give an increased reduction activity. Also, the SCR reaction between stored NO_x and NH_3 influences the height of the NO_x peak. In our detailed kinetic model we found that a SCR reaction between the stored NO_x and ammonia to be very important in order to describe the rich conditions [38]. More specifically, the SCR was crucial to describe the delay in ammonia observed together with 100% selectivity to NH_3 in the end of the rich period (Fig. 4). The importance of a SCR reaction based on experiments is also proposed in the literature [17,44–46]. In our model [38] we propose that it is a reaction between stored NO_x and ammonia. This explains the ammonia delay simultaneously as the 100% NO_x conversion to NH_3 in the end of the rich period. If the reaction occurred between NH_3 and NO in the gas phase, it would also occur in the end of the rich period as well and the conversion of ammonia would be much less than the 100% observed experimentally. Also Nova et al. [45] propose a reaction between stored NO_x and NH_3 . Thus a well-dispersed barium may increase the contact between the barium and platinum and the rate for the SCR reaction would likely benefit from this.

N_2O is produced for all samples in the rich period (Fig. 3) and is visible at the same time as the later part of the NO_x peak. When the

Table 2

N_2 selectivity at 200°C , 300°C , and 400°C .

Sample	200°C (%)	300°C (%)	400°C (%)
Al/Pt/Ba	46	76	74
Al/Pt	40	42	12
Al/Ba/Pt	28	48	27

NO_x and N_2O approaches zero NH_3 is observed. We did not measure N_2 , but our detailed kinetic model predicted the start of the N_2 formation before the NH_3 , which also was observed experimentally by Mulla et al. [46], Nova et al. [45] and Cumaranatunge et al. [44]. An observable feature is the formation of N_2O not only during rich conditions but also in the beginning of the lean period of the Al/Pt sample. A small amount of N_2O is also formed over the Al/Ba/Pt catalysts during lean conditions as well. The N_2O in the lean period over Al/Pt has its maximum at the lowest temperature, with 175 ppm at 200 °C and is only 10 ppm at 400 °C. Our detailed model [38] predicted an N_2 peak in the lean period at 200 °C, which was not present at higher temperatures. This is in line with experimental findings by Lietti et al. [10]. We suggest that the reason is a buildup of hydrogen and ammonia species on the platinum surface during rich conditions, which reacts with the incoming NO_x in the initial part of the lean period, forming a peak of N_2 and N_2O . At higher temperature the coverage of NH_3 and N_2 on Pt is lower, causing less production of N_2O and N_2 .

The measured NH_3 concentrations, displayed in Figs. 4 and 5, show an overshoot of the NH_3 over the inlet NO_x concentration for many of the catalysts examined. This NH_3 is formed from NO_x adsorbed in the lean periods, which also was concluded in Refs. [29,38]. For all catalysts examined the total amount of formed NH_3 and the amount of NH_3 formed from NO_x previously adsorbed is the largest at 200 °C (Table 3). The amount of NO_x in the release curves, which is observed immediately when switching to rich conditions, is lower at 200 °C than the amount measured at higher temperatures. The coverages of hydrogen are higher on Pt at lower temperatures [38], which is beneficial for the NH_3 production. In addition, the SCR reaction is activated and the rate for this reaction will also be higher at higher temperature, resulting in an increased conversion of the NH_3 .

The ammonia formation is evidently influenced by the order of the impregnation steps in the preparation as shown in Figs. 4 and 5. As described above, the delay of the ammonia signal observed was explained by a selective catalytic reduction (SCR) reaction between the ammonia formed and the nitrites/nitrates adsorbed on the catalyst forming nitrogen and water [29,38]. The ammonia is detected in the gas phase when most of the nitrites/nitrates are depleted by the SCR reaction. At 200 °C the amount of stored NO_x is similar for the two barium samples. However, the ammonia is observed earlier from the Al/Pt/Ba than from Al/Ba/Pt. It is possible that there is a higher reduction activity of the platinum in the Al/Pt/Ba sample, due to that Pt is adsorbed on alumina and possibly by a better contact between Pt and barium. This is discussed thoroughly above and may explain both why the reduction is completed and NH_3 is seen earlier using the Al/Pt/Ba sample. At 300 °C the ammonia delay is larger for the Al/Pt/Ba sample and the difference is even more pronounced at 400 °C. This can be explained by the larger NO_x storage of the Al/Pt/Ba sample. At 300 °C the Al/Pt/Ba stores 25% more than the Al/Ba/Pt sample and at 400 °C the difference is 54%.

5. Conclusions

In this paper, the influence of the preparation method on the behavior of NO_x storage and reduction catalysts was studied. Two samples contained Pt, Ba and Al and one sample contained Pt and Al. The catalysts examined were prepared by changing the order of the impregnation steps. The storage capacity of the barium containing samples is significantly influenced by the order of the impregnation steps. It is shown that the storage capacity at higher temperatures is higher for the catalysts prepared by impregnating barium on Al/Pt than by impregnating Pt on Al/Ba and at 400 °C the storage is increased with as much as 54%.

The optimum storage temperature for the Al/Pt/Ba samples occurs around 300–400 °C. The corresponding temperature for the Al/Ba/Pt samples is 200–300 °C, and is similar to Al/Pt (200 °C). 20 wt% results in a maximum coverage of barium on the alumina surface of about 0.75 ML, thus there are alumina sites available for storage. Our NO_2 TPD experiments showed that the storage on alumina is less stable compared to on barium. Further, earlier results have shown that Al/Pt is poisoned by water, but no large effect is observed for CO_2 . For the Al/Pt/Ba catalyst we found that at low temperature the storage is influenced the most by water and at high temperatures of CO_2 . Based on these results we propose that the low temperature stable NO_x species stored on Pt, Ba and alumina containing catalysts occur both on alumina and surface barium.

We suggest that the reason for the shift in temperature for maximum storage and also the high storage at 400 °C for the Al/Pt/Ba sample is that barium is better utilized when it is added to the catalyst after the Pt impregnation than before. This may be due to the negative effect of the platinum precursor on barium during the preparation of Al/Ba/Pt samples, which can lower the dispersion of the barium. This will cause a decrease in the amount of storage sites available and possibly also a decrease in the interfacial area between Ba and Pt for the Al/Ba/Pt samples compared to the Al/Pt/Ba. This can also explain the lowering of BET surface area for the Al/Pt/Ba sample compared to the Al/Ba/Pt, due to blocking more of the alumina pores when barium is more dispersed over the sample.

The regeneration performance of all catalysts examined was also clearly affected by the preparation procedure. The amount of NO_x released was lower for the Al/Pt/Ba sample compared to the Al/Ba/Pt sample. In addition, the selectivity to N_2 was much larger on Al/Pt/Ba. We propose that there is a higher reduction capacity in this catalyst, which may be due to higher activity of platinum, proximity between platinum and barium or a combination between the two. It is possible that the Pt activity in Al/Pt/Ba is higher than when Pt is impregnated on Ba/Al, due to the negative effect of that barium is alkaline. Also, as described above, we propose that the barium is more well dispersed for the Al/Pt/Ba sample, which would lead to a better contact between platinum and barium. This is beneficial both for the reduction of the stored NO_x and likely also for the NH_3 SCR reaction.

Ammonia and N_2O were formed over all catalysts during the rich period. The delay of the ammonia signal is explained by an SCR reaction between the nitrites/nitrates on the catalysts and the ammonia formed. At 200 °C the Al/Pt/Ba and the Al/Ba/Pt stores similar amounts. However, the ammonia signal is observed earlier for the Al/Pt/Ba sample. We suggest that this might be due to a better reduction capacity of the Al/Pt/Ba, due to that Pt is impregnated on alumina and possibly better dispersed barium, facilitating a better contact between Pt and Ba. This would also explain the lowering of the NO_x peak. At 300 °C and 400 °C the ammonia delay is larger for the Al/Pt/Ba sample, likely because at these temperatures the Al/Pt/Ba sample stores significantly more NO_x . In addition, formation of N_2O was observed over the Al/Pt catalysts during the lean period as well as the rich period, which is explained by hydrogen residues on the catalyst still present in the beginning of the lean period.

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References

- [1] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S.-I. Matsumoto, T. Tanizawa, *Catalysis Today* 27 (1996) 63–69.
- [2] E. Fridell, M. Skoglundh, S. Johansson, B. Westerberg, A. Tornqvist, G. Smedler, *Studies in Surface Science and Catalysis* 116 (1998) 537–547.
- [3] H. Mahzoul, J.F. Brilhac, P. Gilot, *Applied Catalysis B: Environmental* 20 (1999) 47–55.
- [4] L. Castoldi, I. Nova, L. Lietti, P. Forzatti, *Catalysis Today* 96 (2004) 43–52.
- [5] M. Piacentini, M. Maciejewski, A. Baiker, *Applied Catalysis B: Environmental* 59 (2005) 187–195.
- [6] M. Piacentini, M. Maciejewski, A. Baiker, *Applied Catalysis B: Environmental* 60 (2005) 265–275.
- [7] P.T. Fanson, M.R. Horton, W.N. Delgass, J. Lauterbach, *Applied Catalysis B: Environmental* 46 (2003) 393–413.
- [8] F. Laurent, C.J. Pope, H. Mahzoul, L. Delfosse, P. Gilot, *Chemical Engineering Science* 58 (2003) 1793–1803.
- [9] S. Balcon, C. Potvin, L. Salin, J.F. Tempere, G. Djega-Mariadassou, *Catalysis Letters* 60 (1999) 39–43.
- [10] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, *Journal of Catalysis* 204 (2001) 175–191.
- [11] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, *Catalysis Today* 75 (2002) 431–437.
- [12] L. Olsson, H. Persson, E. Fridell, M. Skoglundh, B. Andersson, *Journal of Physical Chemistry B* 105 (2001) 6895–6906.
- [13] L. Olsson, E. Fridell, M. Skoglundh, B. Andersson, *Catalysis Today* 73 (2002) 263–270.
- [14] A. Lindholm, N.W. Currier, A. Yezerets, L. Olsson, *Topics in Catalysis* 42–43 (2007) 83–89.
- [15] W.S. Epling, A. Yezerets, N.W. Currier, *Applied Catalysis B: Environmental* 74 (2007) 117–129.
- [16] I. Nova, L. Lietti, L. Castoldi, E. Tronconi, P. Forzatti, *Journal of Catalysis* 239 (2006) 244–254.
- [17] J.A. Pihl, J.E. Parks, C. Stuart Daw, T.W. Root, SAE Tech. Paper 2006-01-3441, 2006.
- [18] S. Poulston, R.R. Rajaram, *Catalysis Today* 81 (2003) 603–610.
- [19] Z. Liu, J.A. Anderson, *Journal of Catalysis* 224 (2004) 18–27.
- [20] P. Jozsa, E. Jobson, M. Larsson, *Topics in Catalysis* 30–31 (2004) 177–180.
- [21] D. James, E. Fourre, M. Ishii, M. Bowker, *Applied Catalysis B: Environmental* 45 (2003) 147–159.
- [22] H. Abdulhamid, E. Fridell, M. Skoglundh, *Topics in Catalysis* 30–31 (2004) 161–168.
- [23] J. Dawody, M. Skoglundh, S. Wall, E. Fridell, *Journal of Molecular Catalysis A: Chemical* 225 (2005) 259–269.
- [24] U. Elizundia, R. Lopez-Fonseca, I. Landa, M.A. Gutierrez-Ortiz, J.R. Gonzalez-Velasco, *Topics in Catalysis* 42–43 (2007) 37–41.
- [25] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, F. Prinetto, G. Ghiotti, *Journal of Catalysis* 222 (2004) 377–388.
- [26] M. Piacentini, R. Strobel, M. Maciejewski, S.E. Pratsinis, A. Baiker, *Journal of Catalysis* 243 (2006) 43–56.
- [27] J. Dawody, L. Eurenus, H. Abdulhamid, M. Skoglundh, E. Olsson, E. Fridell, *Applied Catalysis A: General* 296 (2005) 157–168.
- [28] A. Lindholm, N.W. Currier, E. Fridell, A. Yezerets, L. Olsson, *Applied Catalysis B: Environmental* 75 (2007) 78–87.
- [29] A. Lindholm, N.W. Currier, E. Fridell, A. Yezerets, L. Olsson, *Applied Catalysis B: Environmental* 75 (2007) 78.
- [30] W.S. Epling, J.E. Parks, G.C. Campbell, A. Yezerets, N.W. Currier, L.E. Campbell, *Catalysis Today* 96 (2004) 21–30.
- [31] J. Szanyi, J.H. Kwak, J. Hanson, C.M. Wang, T. Szailer, C.H.F. Peden, *Journal of Physical Chemistry B* 109 (2005) 7339–7344.
- [32] M.H. Kim, J.R. Ebner, R.M. Friedman, M.A. Vannice, *Journal of Catalysis* 204 (2001) 348–357.
- [33] E. Fridell, H. Persson, B. Westerberg, L. Olsson, M. Skoglundh, *Catalysis Letters* 66 (2000) 71–74.
- [34] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, G. Smedler, *Journal of Catalysis* 183 (1999) 196–209.
- [35] P.-H. Han, Y.-K. Lee, S.-M. Han, H.-K. Rhee, *Topics in Catalysis* 16/17 (2001) 165.
- [36] J.H.K.J. Szanyi, D.H. Kim, S.D. Burton, C.H. Peden, *Journal of Physical Chemistry B: Letters* 109 (2005) 27–29.
- [37] B. Westerberg, E. Fridell, *Journal of Molecular Catalysis A: Chemical* 165 (2001) 249–263.
- [38] A. Lindholm, N.W. Currier, J. Li, A. Yezerets, L. Olsson, *Journal of Catalysis* 258 (2008) 273–288.
- [39] C.-W. Yi, J.H. Kwak, C.H.F. Peden, C. Wang, J. Szanyi, *Journal of Physical Chemistry C: Letters* 111 (2007) 14942.
- [40] T.J. Toops, D.B. Smith, W.S. Epling, J.E. Parks, W.P. Partridge, *Applied Catalysis B: Environmental* 58 (2005) 255–264.
- [41] T. Szailer, J.H. Kwak, D.H. Ki, J. Szanyi, C. Wang, C.H. Peden, *Catalysis Today* 114 (2006) 86–93.
- [42] L. Olsson, E. Fridell, *Journal of Catalysis* 210 (2002) 340–353.
- [43] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, *Catalysis Today* 27 (1996) 63–69.
- [44] L. Cumararatunge, S.S. Mulla, A. Yezerets, N.W. Currier, W.N. Delgass, F.H. Ribeiro, *Journal of Catalysis* 246 (2007) 29–34.
- [45] I. Nova, L. Lietti, P. Forzatti, *Catalysis Today* 136 (2008) 128.
- [46] S.S. Mulla, S.S. Chaugule, A. Yezerets, N.W. Currier, W.N. Delgass, F.H. Ribeiro, *Catalysis Today* 136 (2008) 136.